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11

Publication number:

**0 351 054  
A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: 89305880.0

51 Int. Cl.4: **B60C 1/00 , C08L 21/00 ,  
/(C08L21/00,51:04)**

22 Date of filing: 09.06.89

30 Priority: 02.07.88 GB 8815793

43 Date of publication of application:  
17.01.90 Bulletin 90/03

64 Designated Contracting States:  
DE FR GB

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54 Pneumatic tyres.

57 Pneumatic tyres having an improved steering response have a tread portion which comprises a blend of a base elastomer and, as a steering response substance, a polymer of an unsaturated compound selected from methacrylic acid, acrylic acid and lower alkyl esters thereof. The steering response substance is preferably a graft copolymer of isoprene and methylmethacrylate. A preferred amount of the steering response substance is in the range from 5 to 60% by weight of the total of the base elastomer and the steering response substance.

**EP 0 351 054 A1**

## PNEUMATIC TYRES

This invention relates to pneumatic tyres having improved performance on the road; in particular it concerns means of improving steering response or frictional grip on wet road surfaces (referred to herein as "wet grip"). In a preferred form of the invention both steering response and wet grip are improved.

Steering response can be defined as the rate of deviation from the "straight ahead" vehicle position during driving by the application of a small steering input (about 15° of steering wheel revolution or about 0.5° slip angle). It is a very important factor in motor racing. Attempts made in the past to increase steering response (which is closely related to a tyre's cornering stiffness) have been by increasing the stiffness of the tyre compound in general and the tread in particular. However, in this past work it has been found that increasing the compound stiffness results in a corresponding reduction in the wet grip of the resulting tyres for they then have a lower energy absorption potential (loss compliance).

It has now surprisingly been found that by inclusion of certain additives (referred to herein as "steering response substances") the steering response of tyres can be increased substantially without any substantial detrimental affect on wet grip.

Accordingly, in a first aspect the present invention provides a pneumatic tyre whose tread portion comprises a blend of a base elastomer and, as a steering response substance, a polymer of an unsaturated compound selected from methacrylic acid, acrylic acid and lower alkyl esters thereof.

The lower alkyl ester is conveniently one in which the lower alkyl group has 1 to 6 carbon atoms, for example it can be methyl, ethyl, propyl (*n*- or *iso*-) or butyl (*n*-, *iso*-, *sec*- or *t*-). Said ester is conveniently a lower alkyl ester of methacrylic acid, for example it can be methyl methacrylate, and it is with particular reference to the use of methyl methacrylate as the ester that the following description relates.

The steering response substance is conveniently a natural or synthetic rubber (referred to herein as an auxiliary rubber) modified with the lower alkyl ester of methacrylic acid or acrylic acid. For example, the modified rubber can be one obtained by graft or other polymerisation of the rubber with said ester. By way of example, where the auxiliary rubber is a natural rubber, the modified rubber can be a product obtained by graft copolymerisation of the natural rubber with said ester in monomeric form, the graft copolymerisation being effected, for instance, between an emulsion or dispersion of the auxiliary rubber and the ester, the content of the lower alkyl ester in the modified rubber being, for instance, in the range from 5% to 60% (for instance 15, 20, 30, 40, 45 or other proportion in the range 15 to 50%) by weight of the modified rubber.

In producing the tyres of the present invention the steering response substance is used in any convenient proportion in the elastomer composition such that it will, on the one hand, provide a useful increase in steering response of pneumatic tyres whose tread portion comprises the elastomer composition after vulcanisation and, on the other hand, is not sufficiently high as to derogate from the other desirable properties of the composition. Suitable amounts of the steering response substance depend, to some extent at least, on its content of the lower alkyl ester. However, in general, the steering response substance can be used in an amount in the range 5 to 100 parts by weight per hundred parts of rubber, that is of the total weight of the tyre tread polymer (referred to below as the base polymer) and the steering response substance. Where the base polymer is an SBR rubber the amount is preferably in the range from 10 to 50 parts, especially 15 to 30 parts per 100 parts of rubber; where the base polymer is a natural rubber the amount of steering response substance is preferably in the range 10 to 80, especially 15 to 40, 50 or 60 parts per 100 parts of rubber. As can be seen from the Examples below good results have been obtained using 20 parts of the steering response substances referred to as MG30 and MG49 in an amount of 20 parts per 100 parts of rubber.

If desired, the amount of steering response substance can be assessed in terms of the amount of methyl methacrylate (or other lower alkyl ester) in the tyre tread composition. Thus, where as in Example 2 below the steering response substance MG30 is used in an amount of 20 parts per 100 parts of rubber and contains 30% by weight of methyl methacrylate the content of methyl methacrylate in the tread composition is about 6%; the corresponding figure for the use in Example 3 of MG 49 at the rate of 20 parts per 100 rubber is about 9.8% methyl methacrylate content.

The steering response substance can be incorporated in the elastomer composition in any convenient way; however, in general it is incorporated in the composition concurrently with incorporation of the vulcanisation agents and in like manner.

Instead of, or as well as, the lower ester of methacrylic acid or acrylic acid there can be used in this invention methacrylic acid and/or acrylic acid. Thus, for example the steering response substance can be a graft or other copolymer of an auxiliary rubber and methacrylic acid and/or acrylic acid.

The invention is illustrated by the following Examples of which Examples 1 and 4 are control or comparative examples containing no added steering response substance and Examples 2, 3, 5 and 6 are examples of the invention containing a steering response substance.

The base elastomeric polymers used in Examples 1, 2 and 3 and 4, 5 and 6, respectively, were an emulsion SBR and a natural rubber; and the compounding ingredients were chosen so that the compositions of Examples 1 - 3 were suitable for the tread of motor car tyres and the compositions of Examples 4 - 6 for truck tyres. Examples 7 - 12 relate to vulcanised compositions obtained by vulcanising the compositions of Examples 1 - 6 respectively.

In the Examples all "parts" are by weight unless stated to the contrary and the abbreviations used have the following meanings:

MG 30 and MG 49 are each a graft copolymer obtained by graft polymerising methyl methacrylate in natural rubber latex and containing, respectively, nominal proportions of 30 and 49% by weight of poly-(methyl methacrylate). They have been obtained from the Rubber Research Institute of Malaysia, PO Box 150, Kuala Lumpur, Malaysia.

SBR (23% S) -	a styrene-butadiene copolymer having a styrene content of 23% by weight.
SMR 20 -	a natural rubber
N 375 black -	a carbon black
Enerflex 94 -	an aromatic extending oil sold by British Petroleum Company
6PPD -	an antidegradant
TMQ -	an antidegradant
CBS -	cyclohexylbenzthiazyl sulphenamide vulcanisation accelerator

The stearic acid referred to in the Examples was a blend of fatty acids sold for use in the rubber industry and containing fatty acids having nine to 21 carbon atoms in the hydrocarbon chain.

The rubber compositions of Examples 1 to 6 were obtained by blending together in an internal mixer the ingredients as shown in Table 1, and the resulting compositions were moulded into test pieces, the cure being under the conditions referred to below.

The rubber compositions of Examples 2 and 3 have the same constitution as that of the control Example 1 except that they contain 20 parts of MG30 and MG 49, respectively in place of 20 parts of the base polymer. Similarly, the rubber compositions of Examples 5 and 6 have the same constitution as that of Example 4 except that they contain 20 parts of MG 30 and MG 49, respectively in place of 20 parts of the base polymer.

TABLE 1

Example No.	1	2	3	4	5	6
SBR(23%S)	100.00	80.00	80.00	-	-	-
SMR20 (NR)	-	-	-	100.00	80.00	80.00
MG 30	-	20.00	-	-	20.00	-
MG 49	-	-	20.00	-	-	20.00
Zinc Oxide		1.50			4.00	
Stearic Acid		1.00			2.00	
N375 Black		70.00			50.00	
Aromatic Oil		37.50			-	
6 PPD		1.00			1.00	
TMQ		0.50			0.50	
Paraffin Wax		1.00			1.00	
Sulphur		1.80			1.20	
CBS		1.80			1.20	
		216.10			160.90	

EXAMPLES 7 to 12

Part of each of the six rubber compositions of Examples 1 to 6 was moulded into test samples and subjected to vulcanisation conditions comprising 15 minutes while the temperature was raised to 165°C followed by 20 minutes at that temperature. The resulting vulcanised test samples were tested using the dynamic response apparatus described in the paper by J.E. Smith and E.C. Sumner, published in "Proceedings of The International Rubber Conference 1972". The test conditions and the values obtained for complex modulus and loss factor are shown in Table 2 below.

A second part of each of the six rubber compositions of Table 1 was tested to assess its wet grip on a road surface. Each of those compositions was used as the tread compound of model tyres of size 2.25- 8 inches (57 - 203 mm). The tyres were moulded under the following vulcanisation conditions: 60 minutes at 155°C. These model tyres were subjected to two tests as follows:

Grip on a wet Delugrip road surface (Delugrip is a Registered Trade Mark) was measured using the internal drum machine described in a paper by R.J. Blythe published in "Proceedings of The International Rubber Conference", 1986, Gothenburg, Sweden. Measurements of the wet grip were made for peak and locked wheel sliding friction over a range of speeds from 8.9 to 22.4 m/sec. The test was repeated using a Bridport pebble surface instead of the Delugrip surface. The results obtained were normalised relative to the control. The results (together with mean normalised values for the two surfaces) are shown in Table 3.

TABLE 2

Example No.	1	2	3	4	5	6
Dynamic Response						
Apparatus (DRA)						
3% deflection and 15HZ						
Complex Modulus at 23 ° C (MPa)	11.0	12.4	13.9	-	-	-
Loss Factor at 23 ° C	0.40	0.42	0.44	-	-	-
Calculated steering response	6.5	7.0	7.5	-	-	-
Calculated "Wet cornering" (g)	0.58	0.58	0.60	-	-	-
Complex Modulus at 80 ° C (MPa)	-	-	-	6.6	8.4	9.6
Loss Factor at 80 ° C	-	-	-	0.13	0.16	0.17

TABLE 3

Example No.	7	8	9	10	11	12
Wet grip						
(Internal drum)						
Bridport Pebble (Peak)	100	102	104	100	105	108
Bridport Pebble (Locked)	100	104	100	100	110	107
Delugrip (Peak)	100	102	105	100	102	92
Delugrip(Locked)	100	100	103	100	103	105
Mean Rating	100	102	103	100	105	107*

\* excluding Delugrip Peak

From Tables 2 and 3 it will be seen that use of the MG30 and MG49 has resulted in an increase in stiffness and in wet grip, especially where the base polymer natural rubber.

The rheometry of each of the rubber compositions of Examples 7 to 12 is shown in Table 4 below. The meanings and means of calculation of the parameter symbols shown in Table 4 are given in Table 5 below.

TABLE 4

Parameter Symbol	Example No.						Units
	7	8	9	10	11	12	
RHnum	2	2	2	2	2	2	
min	.96	1.14	1.13	2.48	2.67	2.82	N.m
S	6.42	6.67	7.08	4.43	4.48	4.30	mins
T35	7.83	7.83	8.33	5.38	5.47	5.35	mins
T90	13.08	12.25	12.58	7.75	8.00	7.92	mins
CR	.67	.85	.89	1.75	1.73	1.74	N.m/min
MAX-min	5.49	5.77	5.94	6.96	7.25	7.50	N.m
OT	6.45	6.91	7.07	9.44	9.91	10.32	N.m
MT	-	-	-	-	-	-	N.m
RR	0.007	-	-	-	-	-	N.m/min
RI(1)	-	-	-	-	-	-	-
RI(16)	-	-	-	-	-	-	-
T100	22.83	22.67	26.25	13.50	13.58	14.67	mins

TABLE 5

5	<u>Parameter Descriptions</u>			
	<u>Parameter</u>	<u>Symbol</u>	<u>Calculation</u>	<u>Units</u>
10	Plasticity	min	minimum torque	Nm
	Scorch	S	time to min + 0.2265 Nm (+ 2.0 inch lbs)	minutes
	Time to 35% x link density	T35	time to 35% of max-min	minutes
15	Time to 90% x link density	T90	time to 90% of max-min	minutes
	Cure rate	CR	$\frac{0.9 (\text{max-min}) - 0.2265}{T90 - S}$	$\frac{\text{Nm}}{\text{minutes}}$
20	X link density	Max-min	torque at Max - torque at min	Nm
	Optimum torque	OT	maximum torque when reversion occurs	Nm
25	Maximum torque	MT	maximum torque when reversion does not occur	
	<u>NB</u> MT can be at 60, 90 or 120 minutes depending on the time chosen for the compound to be tested.			
30	Reversion rate	RR	$\frac{OT - \text{torque 10 mins beyond OT}}{10}$	$\frac{\text{Nm}}{\text{minutes}}$
35	Reversion index (1)	RI(1)	$\frac{100 (OT - \text{torque at 60 mins})}{OT - \text{min}}$	-
	Reversion index (16)	RI(16)	$\frac{100 (OT - \text{torque at 16 hours})}{OT - \text{min}}$	-
40	Time to optimum torque	T100	required for computing T100+10 mins for reversion rate calculation	

45 **Claims**

1. A pneumatic tyre whose tread portion comprises a blend of a base elastomer and, as a steering response substance, a polymer of an unsaturated compound selected from methacrylic acid, acrylic acid and lower alkyl esters thereof.
2. A pneumatic tyre according to Claim 1, in which said polymer is a copolymer.
3. A pneumatic tyre according to Claim 2, in which said copolymer is a graft copolymer of isoprene and said unsaturated compound.
4. A pneumatic tyre according to Claim 3, in which said copolymer has been obtained by a process of subjecting a rubber to graft polymerisation with said unsaturated compound.
5. A pneumatic tyre according to Claim 4, in which the rubber is natural rubber latex.
6. A pneumatic tyre according to any of the preceding claims, in which said unsaturated compound is methyl methacrylate.
7. A pneumatic tyre according to Claim 1, in which the steering response substance is present in the

blend in an amount of from 5 to 60% by weight of the total of said base elastomer and the steering response substance.

8. A pneumatic tyre according to Claim 7, in which said amount is in the range from 15 to 50% by weight.

5 9. A pneumatic tyre according to Claim 1, in which said blend comprises: (a) an SBR elastomer or a cis-1,4-polyisoprene as the base polymer, and (b) a graft copolymer of isoprene and methyl methacrylate as the steering response substance, said graft copolymer constituting from 10 to 40% by weight of the total of said base elastomer and the steering response substance.

10 10. A pneumatic tyre according to Claim 6, in which the amount of poly (methyl methacrylate) in said blend is in the range from 3 to 20% by weight of the total of said base elastomer and the steering response substance.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DATABASE CHEMICAL ABSTRACTS, vol. 79, no. 4, 1973, abstract no. 20012q, Columbus, Ohio, US; A.V. SHILKIN et al.: "Use of liquid rubbers for modification of rubber vulcanizates", & PROIZVOD. SHIN, REZINOTHEKH. ASBETOTEKH. IZDELII, REF. SB., NO. 1, 6-8 * Abstract * ---	1-2	B 60 C 1/00 C 08 L 21/00 // (C 08 L 21/00 C 08 L 51:04 )
A	EP-A-0 149 836 (HOECHST) * Claims 1,7 * ---		
A	DATABASE CHEMICAL ABSTRACTS, vol. 103, no. 16, 1985, abstract nr. 124803d, Columbus, Ohio, US; & JP-A-60 72 940 (YOKOHAMA RUBBER CO.) 25-04-1985 * Whole document * ---		
A	DATABASE CHEMICAL ABSTRACTS, vol. 89, no. 18, 1978, abstracts nr. 147893q, Columbus, Ohio, US; M.A. WHEELANS: "Hard flexible materials based on blends of natural rubber with Heveaplus MG 49", IND. GOMMA, 22(4), 51, 53-4 * Whole document * -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-10-1989	Examiner VAN HUMBEECK F.W.C.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same parent family, corresponding document			

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